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Title: Understanding the U3Si2 crystal structure evolution as a function of temperature by neutron diffraction and simulation

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2019 Accomplishments Report Template

Due to popular demand, “type” in text boxes have been removed from the 2019 template. Please send your AFC report submission via email using the following format. Finished reports should only be about two pages long including photos, figures and graphics. See specific instructions for submitting photos, figures and graphics below.

Send report to Heather Medema at Heather.Medema@inl.gov.

Questions? Contact Kate Richardson; kate.richardson@inl.gov , (208) 526-4185 or Heather Medema; heather.medema@inl.gov, (208) 526-7610.

1. **Title (from outline):** Understanding the U_3Si_2 crystal structure evolution as a function of temperature by neutron diffraction and simulation
2. **Principal Investigator:** Sven C. Vogel/LANL
3. **Team Members/ Collaborators:** Tashiema L. Ulrich/USC, Joshua T. White/LANL, David A. Andersson/LANL, Elizabeth Sooby Wood/UTA
4. **Introduction:** Provide a brief introduction to the research. (50–150 words).
   U_3Si_2 is actively researched as an accident tolerant fuel. Detailed knowledge of the crystal structure evolution, including knowledge of the anisotropic tetragonal lattice parameters, as a function of temperature and chemical composition is of paramount importance for predictions ranging from thermo-mechanical stresses to phase transformations to crystal lattice sites of fission products. Knowledge of the stability range of U_3Si_2 is of great importance to understand whether changes of the stoichiometry, either from burn-up or due to synthesis variations, will lead to undesirable phase decomposition. To investigate these topics, stoichiometric $U_3Si_{2.00}$ and hyper-stoichiometric $U_3Si_{2.01}$ were synthesized and characterized at ambient conditions and up to 1150°C using time-of-flight neutron diffraction on the HIPPO instrument at the Los Alamos Neutron Science Center (LANSCE) at LANL.

5. **Project Description:** Describe the technical objectives of the research and the benefits to the state-of-knowledge if successful. Also explain how this research is helping DOE meet its objectives of safe, reliable, and economic operation of the nation's current reactor fleet and next generation reactors. (200–300 words).
Understanding the changes in behavior of U_3Si_2 in case of deviations from the line compound are of paramount importance for the application of this system as fuel. Initial thermodynamic calculations (Middleburgh et al., 2016) indicated that the material at room temperature cannot accommodate any significant excess Si atoms, resulting in precipitation of secondary phases. Such a behavior could ultimately affect fuel pellet integrity. More recent calculations revised these earlier results and predict a significant ability of U_3Si_2 to accommodate excess Si atoms without partitioning of secondary phases (Andersson et al., 2018). Ultimately, experimental data is needed to assess this issue and this research provides this data. 12 hours neutron count times (compared to the usual 30-120 minutes) were applied to characterize stoichiometric $U_3Si_{2.00}$ and hyper-stoichiometric $U_3Si_{2.01}$ at room temperature. The ultra-high statistical quality of the diffraction data allowed to assess whether secondary phases were present at a level of >0.1 wt. %. Crystallographic techniques such as difference Fourier maps applied to these data sets allow to identify sites of scattering density unaccounted for by the standard U_3Si_2 crystal structure. These sites are indicative for locations of excess Si atoms, which can subsequently be compared to DFT predictions of these sites. Adding small site occupations of Si atoms to the data analysis model allows then to identify which site fits the experimental data best. The same samples were heated to ~1150°C to assess possible differences in the crystal structure evolution as a function of temperature. Differences in the thermal expansion for different chemical compositions could lead to thermal stresses, which ultimately may lead to cracking of pellets.

6. **Accomplishments:** Summarize the technical goals of the research and the accomplishments made toward these technical goals through September 30, 2017 (end of fiscal year). **Please write all accomplishments in narrative form.** (300–500 words)

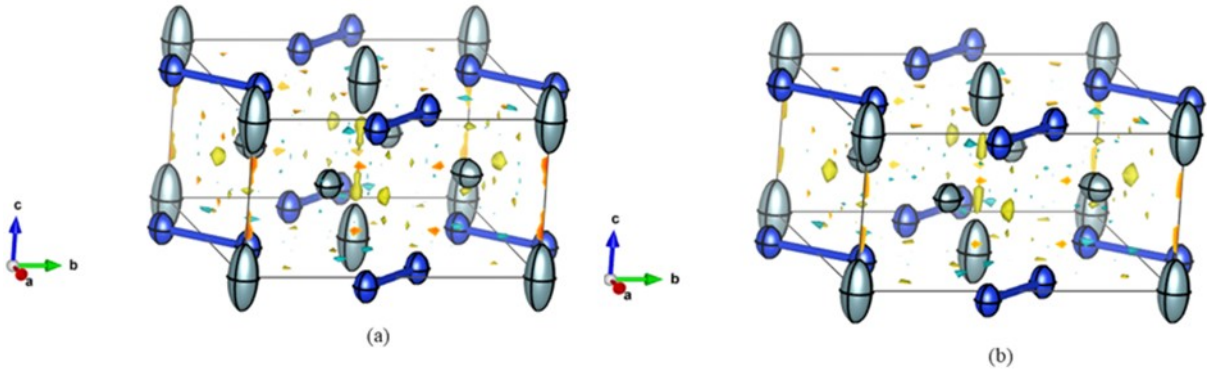
Include contributions by all parties, naming the institution and, where appropriate, individuals involved.
The stoichiometric $U_3Si_{2.00}$ and hyper-stoichiometric $U_3Si_{2.01}$ were synthesized at LANL's Fuel Research Lab by J. White (LANL) and E. Sooby Wood (now UT Austin) by arc-melting of weighed amounts of the constitutive elements. Because uranium metal readily oxidizes, great care was taken to control the oxygen in the atmosphere, e.g. by use of oxygen getters. The ingot was crushed into a powder, sieved, annealed, and then loaded into vanadium cans for the neutron diffraction experiments (vanadium has a typically negligible contribution to the diffraction signal). Neutron diffraction data was collected at ambient conditions for ~12 hours per sample as well as in a vanadium furnace at temperatures up to 1150°C (S. Vogel/LANL). The neutron diffraction data was analyzed using the Rietveld method by T. Ulrich (University of South Carolina, Columbia) and S. Vogel (LANL). The neutron diffraction data analysis provided lattice parameters of the tetragonal unit cell, atom positions of the uranium and silicon atoms, and anisotropic atomic displacement parameters as a function of temperature. Significant differences in volume expansion as well as thermal expansion along the a and c-axes was found for the two compounds. The anisotropic atomic displacement parameters showed an approximately five times larger thermal motion along the crystallographic c-axis than along the a-axis for one of the two uranium sites while the second uranium site and the silicon atom showed an approximately spherical atomic displacement at all temperatures investigated. From the unit cell and atom position parameters, the bond lengths could be computed as a function of temperature. The bond length allowed to compute strains, identifying stronger and weaker bonds within the unit cell. At no temperature were any additional phases observed. The analysis of the difference Fourier map from the high-quality ambient condition runs revealed scattering density not accounted for in the stoichiometric crystal structure. Adding Si atoms on those sites, with partial occupancy, allowed to identify the best match to the experimental data. Occupation of the 4e site (½, ½, 0.262) was identified as the most likely site of excess Si atoms in the U_3Si_2 structure. D. Andersson (LANL, in collaboration with the NEAMS and CASL programs) predicted the energy of various interstitial sites using DFT calculations, which allowed to confirm the experimental finding. Identification of a site where U_3Si_2 can accommodate excess Si can explain why precipitation of additional phases is not observed. Absence of this precipitation due to excess Si makes the U_3Si_2 system more robust against deviations from stoichiometry, an important finding for the application as a nuclear fuel. However, the observation that the thermal expansion changes significantly if the stoichiometry varies could lead to thermal stresses within a pellet that could ultimately lead to cracking. Further investigations are therefore warranted. The detailed experimental and simulation results were submitted to Journal of Applied Crystallography.

7. **Publications:** Include journal and textbook reports. **List the citations in text form here.** Only publications from the current fiscal year will be included in the annual report.
Vogel, Sven C., Tashiema Lixona Wilson, and Joshua Taylor White. Crystal Structure Evolution of U-Si Nuclear Fuel Phases as a Function of Temperature. No. LA-UR-18-28584. Los Alamos National Lab.(LANL), Los Alamos, NM (United States), 2018.
Tashiema L. Ulrich, Sven C. Vogel, Joshua T. White, David A. Andersson, Elizabeth Sooby Wood, and Theodore M. Besmann, Temperature-Dependent Crystal Structure of U_3Si_2 by High Temperature Neutron Diffraction, submitted to

Acta Materialia.
Sven C. Vogel, Tashiema L. Wilson, Elizabeth Sooby Wood, Joshua T. White, Theodore M. Besmann, Temperature-Dependent Crystal Structure of U_3SI_2 by High-Temperature Neutron Diffraction, accepted for publication in Proceedings of Global/Top Fuel 2019, September 22-26, 2019, Seattle, WA.
Tashiema L. Wilson, T.M. Besmann, S.C. Vogel, J.T. White, Crystal Structure Characterization of Uranium- Silicides Accident Tolerant Fuel by High Temperature Neutron Diffraction, accepted for publication in Advances in X-ray Analysis, **63**, (2019) Proceedings of the 68th Denver X-ray Conference, Lombard, Illinois, U.S.A. 8/5 – 8/9 2019..

8. **Write one sentence on why this project is important.** What is the "wow" factor? This will become one of the call-outs on your project pages so it is not a quote, just something you would like brought to the attention of the reader (e.g., "The transmutation fuel package has supplied fuel samples for thermal and microstructure characterization as well as the fuel and assembly of the AFC-3F irradiation test.)
The combination of high-quality neutron diffraction data and DFT calculations allowed to identify interstitial sites for Si atoms in the U_3Si_2 structures that explains the absence of secondary phases in hyper-stoichiometric U_3Si_{2+1}.

9. **Photos/ Figures/ Graphics.** Please send photos, figures and graphics in separate email(s) from report content. You may submit up to four pertinent, high-quality graphics/photos (**High-resolution, 300 dpi, .jpeg, .tif, .pdf, and eps file formats only)**. At least one picture with researcher(s) is encouraged. Name the photos, figures, and graphics submitted via email according to the name of the Principal Investigator's name followed by sequential photo number for appearance in your report. Then label captions using this name_numbering system in the report content as well (example shown below) so that editors can easily match your emailed images with the captions in your report content.



Name of Project PI_1: Visualization of the refined crystal structure of $U_3Si_{2.00}$ (a) and $U_3Si_{2.01}$ (b) samples including anisotropic atomic displacement parameters at ambient temperature. Overlaid with the crystal structure are the difference Fourier maps for ~60% of the maximum density (yellow positive difference, blue negative difference). The uranium atoms are shown in grey, with U1 on the corners of the tetragonal unit cell, while Si atoms are shown in blue. The identified 4e site for excess Si atoms is between the U1 atoms.

Name of Project PI_2: Caption

Name of Project PI_3: Caption

Name of Project PI_4: Caption